



A highly efficient process for transforming methyl mercaptan into hydrocarbons and H₂S on solid acid catalysts

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ABSTRACT

The catalytic conversion of CH₃SH and CH₃SCH₃ (DMS) on protonic zeolites H-ZSM-5, H-Y and H-ferrierite was studied in a gas flow reactor from 423 to 823 K. Below 700 K, CH₃SH is converted at equilibrium into DMS and H₂S. Above 700 K, light alkanes (C1–C3), benzene, toluene and xylene appear alongside H₂S in the gas phase, and a carbonaceous deposit builds up on the catalyst. DMS is assumed to be the intermediate in the CH₃SH transformation into H₂S and hydrocarbon species. At 823 K, the CH₃SH conversion is total on H-ZSM-5, and only partial on H-Y and H-ferrierite. These are selective to alkanes, and produce large quantities of coke. In contrast, much less coke builds up on H-ZSM-5, which is also more selective to aromatics. After calcination in air flow at 823 K, the spent H-ZSM-5 sample recovers the properties of the fresh catalyst. Similarities and differences with the methanol-to-hydrocarbons process are discussed.

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1. Introduction

Natural gas always contains contaminants or other unacceptable substances including carbon dioxide, hydrogen sulfide, water, carbonyl sulfide, mercaptans, heavy hydrocarbons and mercury [1]. Conditioning natural gas for marketing generally requires the removal of these contaminants, which involves several major operations, among them solvent deacidification, glycol dehydration or molecular sieves, and gasoline extraction. Usually, the treated gas contains minor amounts of contaminants: 2% CO₂, 2–4 ppm H₂S and 5–30 ppm total sulfur (mercaptans and COS). With the increasingly stringent environmental regulations, the technical requirements for further catalytic processes (e.g. syngas fabrication) and the specificities of newly discovered gas deposits with a mercaptan concentration range substantially higher than those hitherto known, the demand for more complete desulfurization is rising. Moreover, it is preferable for industrial and domestic users of natural gas to have mercaptan concentrations lowered into the 1–5 ppmv range. Modern processes for the more complete removal of mercaptans and COS are generally based on fixed-bed adsorption and chemical reactions, the latter generally following the former once the adsorption bed has been stripped. However, it is difficult to remove substantial quantities of mercaptans from a loaded gas stream.

The chemical processes used for the near complete removal of mercaptans may include oxidation, alkaline treatment [2], reaction with olefins [3] and hydrodesulfurization [4]. These all call for additional reagents some of which produce dialkylsulfides or disulfides. MEROX is the most popular of these processes [5]: mercaptans are transformed by caustic washing into mercaptides, which in turn are oxidized to become dialkyldisulfides with soda regeneration.

There are sound economic and ecological benefits to be gained in developing new methods that do not require the addition of any reagents (O₂, H₂, olefins, ...) and produce only low waste. This study focuses on the catalytic conversion of methyl mercaptan into hydrocarbons and H₂S (CH₃SH → Hydrocarbons + H₂S). Because H₂S can be efficiently captured by absorption using conventional solvents such as amines, this chemical transformation (called Methyl Mercaptan To Hydrocarbons, M2TH throughout the remainder of this article) may be considered a key step for achieving the near-complete removal of methyl mercaptan from industrial streams and gas deposits.

Note that the open literature [6–9] offers scant data and no substantial in-depth discussion concerning the catalytic conversion of methyl mercaptan.

As a general comment, the M2TH process may have several points in common with the methanol-to-hydrocarbons process (MTH) [10,11]. Because MTH is highly dependent on the zeolite structure, the M2TH process was carried out on protonic zeolites of different topologies: H-ZSM-5, H-Y and H-ferrierite. The first has the MFI-type structure, characterized by a 2D channel distribution and 10-membered ring pores (5.3 × 5.6 Å). H-Y (FAU topology) is a

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Table 1
Main characteristics of the catalysts.

Catalysts	Si/Al	Main pore size (Å)/pore system ^a	Surface _{BET} (m ² g ⁻¹)	Micropore volume (mL g ⁻¹)	Acid sites ^b (mmol g ⁻¹)
H-ZSM-5	15	5.3 × 5.6/2D	430	0.123	1.31
H-ferrierite	10	5.4 × 4.2/1D	360	0.131	1.82
H-Y	15	7.4 × 7.4/3D	800	0.238	0.89

^a Pore network system: 1D, unidirectional; 2D, bidirectional; 3D, tridirectional; from Atlas of zeolite structures [http://www.iza-structure.org/default.htm].

^b The number of acid sites was determined from the amount of NH₃ desorbed in TPD experiments.

widely open zeolite exhibiting a 3D network of pores delimited by a 12-membered ring featuring large cages (12 Å) that are interconnected through windows of ca. 7.4 Å. H-ferrierite (FER topology) has a 1D, 10-membered ring channel structure (5.4 × 4.2 Å) connected through cages and windows of 8-membered rings (3.8 Å). The main characteristics of the catalysts are given in Table 1.

2. Experimental

2.1. Catalysts and chemicals

Commercially purchased zeolites (Zeolyst) were calcined in air for 5 h at 823 K to obtain their hydrogen form. The powdered materials were pressed, crushed and sieved to keep the grain size at 100–150 μm. The catalysts were stored in an oven at 400 K. Tanks of N₂, CH₃SH/N₂ (5.0/95.0, v/v) and CH₃SCH₃/N₂ (0.5/99.5, v/v) were supplied by Air Liquide.

2.2. Characterization

XRD diffractograms of the zeolites were recorded on a Bruker D8 advance instrument with a copper X-ray source at a voltage of 40 kV and amperage of 40 mA. The system was upgraded with a Lynx Eye detector. All zeolite samples exhibited good crystallinity and the characteristic pattern of their structure.

The porous structure of catalytic materials was studied by N₂ sorption, at 77 K with a Micromeritics ASAP 2010 sorptometer. Before analysis, the samples were desorbed in a vacuum at 573 K for 10 h. The apparent surface area (determined by applying the BET equation) and micropore volume were determined from the N₂ isotherm.

The number of acid sites was evaluated by temperature-programmed desorption (TPD) of ammonia using an AUTOCHEM 2910 (Micromeritics). Before NH₃ adsorption, 100 mg of zeolite was pre-treated in an air flow (30 mL min⁻¹) at 823 K (ramp 10 K min⁻¹) for 30 min. NH₃ adsorption was done at 373 K by exposure to NH₃/He (5.0/95.0, flow rate: 30 mL min⁻¹) for 45 min and then flushed with He (30 mL min⁻¹) for 2 h to remove any NH₃ remaining in the gas phase and physisorbed on the catalyst surface. Finally, ammonia was desorbed in a helium flow (30 mL min⁻¹) from 373 to 923 K at a heating rate of 10 K min⁻¹ and quantified with a thermal conductivity detector (TCD). The profiles of NH₃ desorption are shown in Fig. 1.

To characterize the coke deposit in the catalyst, the microreactor was flushed with nitrogen at 823 K at the end of the reaction, in order to desorb any adsorbed species on the surface of the catalyst. 20 mg of the spent catalyst were then analyzed by thermogravimetry (TGA) with a NETZSCH TG 209C apparatus. The temperature program started with an isothermal period of 5 min at 298 K, and continued with a temperature ramp-up to 1173 K at 5 K min⁻¹ in air (Fig. S1, supplementary information). The weight loss between 723 and 1023 K was considered attributable to the burning of coke. Coke deposited on the catalyst was also examined by IR spectroscopy. DRIFT experiments were carried out with a Bruker IFS 55 spectrometer equipped with a Thermo Spectra Tech reacting cell. Sample aliquots (16 mg) of a mixture in KBr (catalyst/KBr = 20/80 w/w) of

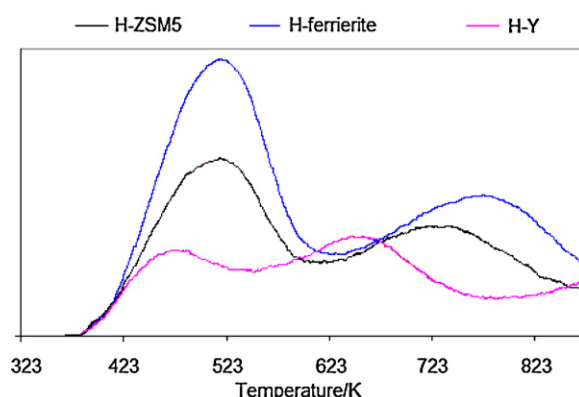


Fig. 1. Ammonia-TPD profiles of catalysts.

the fresh and spent catalysts were activated in situ at 453 K in Ar flow, before examination. The recorded IR spectra are shown in Fig. S2 (supplementary information).

The main characteristics of the catalysts are given in Table 1.

2.3. Catalytic tests

The catalytic conversions of CH₃SH and CH₃SCH₃ (DMS) were carried out in a stainless steel fixed-bed microreactor (4 mm i.d.) at atmospheric pressure, between 423 and 823 K. The composition of the reactor feed was adjusted with flow meters, using the following gases: CH₃SH/N₂ (5/95), CH₃SCH₃/N₂ (0.5/99.5) and N₂. Standard experiments were performed with a bed of 100 mg catalyst supported by glass wool. Quartz powder was used to reduce the volume of the reactor. The conversions of CH₃SH/N₂ (0.5/99.5, v/v, flow: 50 mL min⁻¹) and CH₃SCH₃/N₂ (0.25/99.75, v/v, flow: 20 mL min⁻¹) were carried out at weight hourly space velocities (WHSV, mass_{CH₃SH}/mass_{catalyst} h) of 0.32 and 0.08 h⁻¹, respectively.

The products were analyzed online by gas chromatography (Shimadzu, GC 2014) using an auto-sampling valve. The GC was connected to a dual detector device, flame ionization detector (FID) and flame photometric detector (FPD). To achieve good separation of the compounds and avoid signal saturation at the FPD, a dual-column device was used. After a first Supel-Q™ PLOT column (30 m length × 0.53 mm i.d.), a fused silica “Y” capillary connector split the flow to the FID and to a second column (DB-17 Agilent J&W, 15 m length × 0.25 mm i.d.). The FPD is located after this second column. The conversion was obtained based on the CH₃SH and CH₃SCH₃ consumptions, calculated from input and output concentrations.

3. Results and discussion

In a blank experiment carried out without any catalyst, both CH₃SH and CH₃SCH₃ were converted by only 3% at 773 K. In the presence of zeolites high conversions were obtained at temperatures superior to 573 K. Fig. 2 shows the conversion of CH₃SH and the concentrations of reaction products as a function of temperature with H-ZSM-5 as catalyst.

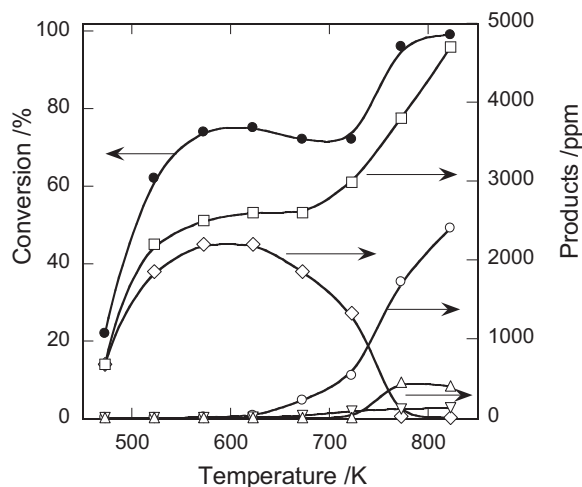


Fig. 2. Conversion of methylmercaptan as a function of temperature on H-ZSM-5. (●) Conversion; (□) H₂S; (◇) DMS; (○) CH₄; (▽) C₂H₆; (△) BTX.

Below 673 K, CH₃SH is selectively converted into comparable amounts of CH₃SCH₃ and H₂S according to the reaction:



From 573 to 673 K, the CH₃SH conversion was 70–75%, which merely corresponds to the equilibrium conversion according to Mashkina et al. [12]. Above 673 K, the CH₃SH conversion improves, achieving nearly full conversion at 823 K. The amount of DMS gradually decreases in favor of methane, ethane and propane (C1–C3), as well as benzene, toluene and xylene (BTX). Methane represents more than 90 vol% in C1–C3. At 823 K, there is no more DMS.

To judge from these results, it is very likely that DMS is the intermediate in the M2TH process. To prove this, catalytic tests with a feed of DMS in N₂ stream (0.25/99.75, v/v) were performed on H-ZSM-5. Fig. 3 shows the conversion of DMS and the product distribution versus temperature. Below 700 K, DMS conversion is low, and only trace amounts of CH₃SH, CH₄ and H₂S were identified. From 723 K, DMS conversion increases very fast with the formation of C1–C3, BTX and H₂S, confirming that DMS is an intermediate in M2TH at high temperature.

Based on these experimental results, a schematic reaction pathway for the transformation of CH₃SH on protonic zeolite at different temperatures is suggested in Scheme 1. A direct transformation of

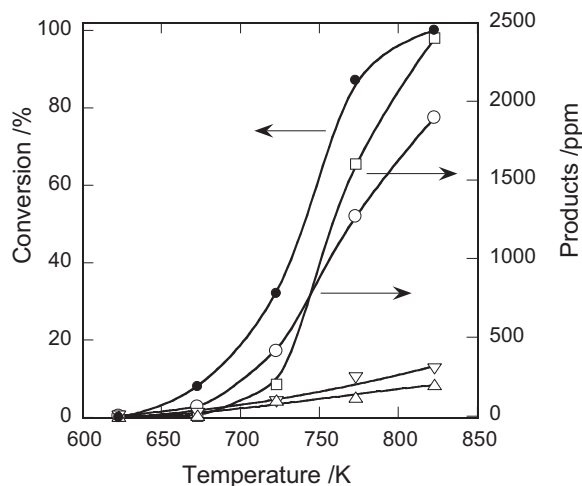
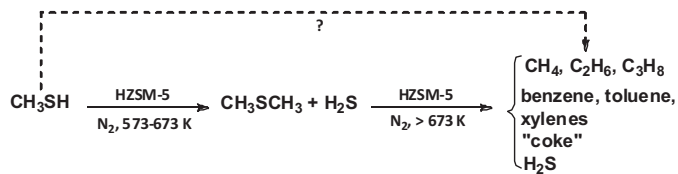


Fig. 3. Conversion of dimethylsulfide as a function of temperature on H-ZSM-5. (●) Conversion; (□) H₂S; (○) CH₄; (▽) C₂H₆; (△) BTX.



Scheme 1. Pathways of the catalytic transformation of CH₃SH into hydrocarbons on H-ZSM-5.

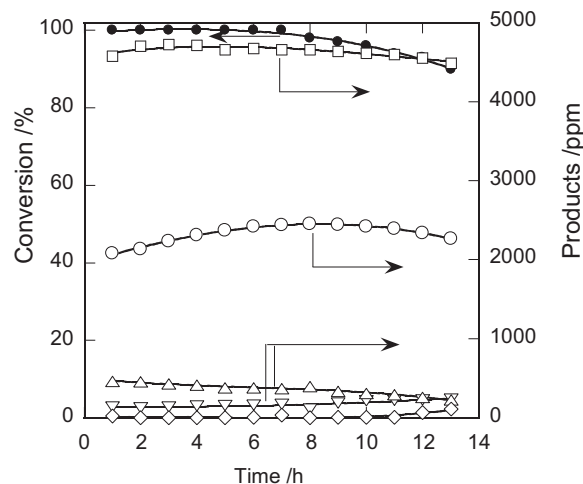


Fig. 4. Conversion of methylmercaptan as a function of time at 823 K on H-ZSM-5. (●) Conversion; (□) H₂S; (◇) DMS; (○) CH₄; (▽) C₂H₆; (△) BTX.

CH₃SH to the final products may occur, but cannot be proved with certainty at this stage.

The catalytic experiments discussed above were carried out in the TPSR mode, in which the temperature of reaction was ramped between 473 and 823 K. To gain better insight of the exact amounts of products formed, and of the catalyst deactivation, long-term experiments (13 h time-on-stream) were carried out at 823 K in the presence of three zeolites. Figs. 4–6 display such runs performed with H-ZSM-5, H-Y and H-ferrierite, respectively. Accordingly, very clear differences in catalytic properties appear and H-ZSM-5 turns out to be the most efficient catalyst with full CH₃SH conversion and high resistance to deactivation. Indeed, on H-ZSM-5, a CH₃SH conversion of 99–100% is maintained for 7 h before declining smoothly with the appearance of DMS. Moreover, during the first 10 h, the only carbon-containing products appearing in the gas phase are

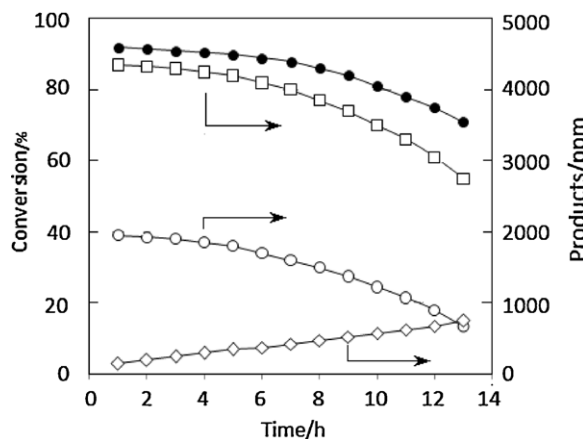


Fig. 5. Conversion of methylmercaptan as a function of time at 823 K on H-Y. (●) Conversion; (□) H₂S; (◇) DMS; (○) C1–C3.

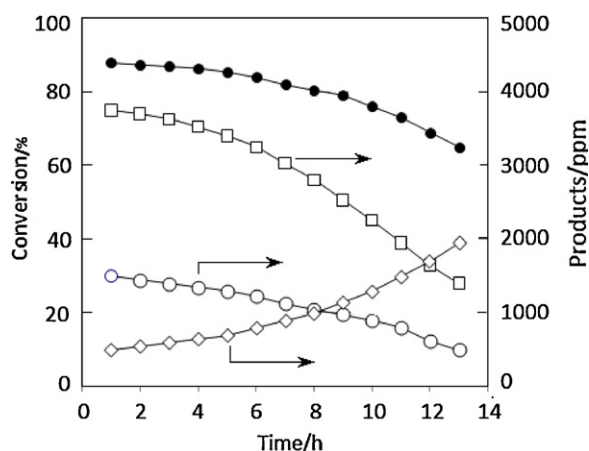


Fig. 6. Conversion of methylmercaptan as a function of time at 823 K on H-ferrierite. (●) Conversion; (□) H₂S; (◇) DMS; (○) C1–C3.

C1–C3 alkanes and BTX. After this period, increasing amounts of DMS are present among the products. In contrast, on H-Y and H-ferrierite the total CH₃SH conversion was about 90% at the beginning of the process, and it decreased rapidly suggesting a fast deactivation of these catalysts. In addition, on both zeolites, a significant amount of DMS is formed for the whole reaction period and only small amounts of aromatics BTX (not shown in Figs. 5 and 6) are produced.

The amount of carbon transformed from CH₃SH into different hydrocarbons, together with the amount of carbon in the products formed, C1–C3 and BTX, were summed over the 13-h period (Table 2).

For instance, with H-ZSM-5, 54 and 44 mg of carbon are formed in C1–C3 and BTX products, respectively. They represent 91% of the amount of carbon transformed from CH₃SH (103 mg), excepting DMS. The missing amount of carbon may be explained by a carbonaceous deposit (called coke) that builds up at the surface of the catalyst. This is corroborated by the black color of H-ZSM-5 after the 13-h operation. The amount of coke on the catalyst determined by TGA was 8.2 mg (Fig. S1, supplementary information, Table 2).

Considering the initial CH₃SH and the three groups of final products (C1–C3, BTX, “coke”), the carbon is equally balanced ($100 \pm 4\%$) for the three catalysts (Table 2). However, very clear differences in catalytic properties appear. H-ZSM-5 is turns out to be the most efficient catalyst, with full CH₃SH conversion into C1–C3, BTX and coke. It is important to note that for the overall period of 13 h, the CH₃SH conversion into the final products only, C1–C3, BTX, “coke”, was about 99, 67 and 40% on H-ZSM-5, H-Y and H-ferrierite, respectively.

It is well known in the MTH process that the distribution between the gaseous products (alkanes, alkenes, aromatics) and the rate and nature of coke formation depends on the pore structure of the zeolites [10,11,13–15]. Table 2 presents the CH₃SH conversion and the amounts of carbon obtained from CH₃SH after 13 h of operation. As shown in Table 2, the selectivity in M2TH (expressed

on a carbon basis) also depends on the zeolite topology. H-Y and H-ferrierite selectively yield alkanes and “coke”, and only small amount of aromatics. In contrast, H-ZSM-5 produces a smaller quantity of “coke” and a large amount of aromatics. This behavior is comparable to that observed in the MTH process: H-ZSM-5 is well known for the formation of aromatics, while the ferrierite topology favors light olefins [11]. On the other hand, one of the major advantages of H-ZSM-5, compared with other zeolites in both MTH [10,14,16] and M2TH processes is its high resistance to deactivation by coke formation. The fast deactivation of H-Y and H-ferrierite in M2TH could be attributed to the large amounts of “coke” produced on these catalysts, most probably from the primary aromatic compounds.

Generally, in the MTH process, the activity correlates with the number and strength of the acid sites. According to ammonia TPD data, H-ferrierite, H-ZSM-5, and H-Y exhibited 1.8, 1.2 and 0.9 mmol g^{−1} acid sites, respectively (Table 1). Moreover, the strength of the acid sites varies in the same order (Fig. 1). Based on the present results, there is no evident correlation between the acidity of zeolite and its activity in the M2TH process.

In spite of some similarities, major differences stand out between M2TH and MTH:

- (1) CH₃SH needs high temperatures to be converted into hydrocarbons. By contrast, methanol is much more easily converted into dimethyl ether (DME) and hydrocarbons. For instance, more than 90% of methanol is converted into DME and hydrocarbons on H-ZSM-5 at only 523 K, while at 644 K, the methanol is totally transformed into hydrocarbons [6].
- (2) A substantial amount of light olefins are formed in the MTH process (ethene, propene), but no olefin was identified in the M2TH process. As is known, the formation of olefins in MTH is supported by what is called the “hydrocarbon pool” (HP) [11,17,18]. According to this mechanism, the hydrocarbon pool species (methylbenzenes and linear alkenes) trapped within the pores of catalysts undergo successive methylation steps by methanol and/or dimethyl ether and eliminate further light olefins.

The absence of light olefins in M2TH, in comparison with MTH, can be understood considering that methylbenzenes (toluene, xylenes) are indeed formed in the presence of H-ZSM-5 during M2TH, but there is nothing in the literature to show that methyl mercaptan is able to methylate aromatic species in order to continue the hydrocarbon pool cycle and liberate light olefins. Speculating, we might interpret the present results as further support for the HP mechanism in the methanol-to-olefins process.

In this study we have not investigated in great detail the nature of the coke formed in the M2TH process. However, attempts were made to obtain some kind of identification using the method described by Nassionou et al. [19]: after dissolution of the mineral matrix of the spent catalysts with diluted HF, a liquid extraction was carried out with CH₂Cl₂. No aromatic compound was detected by GCMS analysis. On the other hand, DRIFT spectroscopy of the used catalysts showed a band at 1590 cm^{−1} characteristic

Table 2
Catalytic behavior of zeolites in the methyl mercaptan decomposition at 823 K.^a

Catalyst	CH ₃ SH conversion ^b (13 h)		DMS ^c /ppm	C amount in products/mg			C balance/%	Product selectivity/%		
	Average/%	C amount/mg		C1–C3	BTX	“Coke”		C1–C3	BTX	“Coke”
H-ZSM-5	98	103	<20	54	44	8.2	103	50.9	41.5	7.6
H-Y	67	50.5	380	29.5	4.1	14.8	96	60.8	8.6	30.6
H-ferrierite	40	32	1050	18.5	2.0	11.5	100	57.8	6.3	35.9

^a Amounts of carbon transformed from CH₃SH into products after 13 h.

^b Conversion into C1–C3, BTX, “coke”.

^c DMS not fully converted to hydrocarbons and “coke”, average value over 13 h.

of polyaromatic species, without any clear C–H stretching band at ca. 3050 cm⁻¹ (Fig. S2, supplementary information). One can reasonably conclude that the coke is highly condensed, with a graphite-like structure.

It is obvious that the viability of this new M2TH process depends directly on the long-term use of the catalyst. The efficiency of a regeneration process was therefore evaluated on the used H-ZSM-5. It consists of air calcination from 523 to 823 K by 50-K, 30-min steps. The regenerated catalyst exhibits catalytic properties that are very similar to the original. Moreover, five successive reaction/regeneration steps were carried out without any difference in the catalytic tests.

4. Conclusions

This work demonstrates that CH₃SH can be successfully converted at high temperatures in the presence of protonic zeolites (H-ZSM-5, H-Y and H-ferrierite) without requiring the addition of any reagent. Below 700 K, CH₃SH is converted at equilibrium into DMS and H₂S, but above 700 K it is selectively converted into H₂S and hydrocarbons (essentially light alkanes and aromatics). ZSM-5 zeolite exhibited the highest activity and stability toward deactivation among the catalysts tested in this catalytic application. In our view, the results reported in this study may be very useful in designing a viable process for cleaning natural gas. Thus, the conversion of mercaptans into hydrocarbons and H₂S over H-zeolites, without any reagent, could be incorporated, as a central stage, into an integrated system comprising well-known technologies, such as the adsorption of mercaptans on solids [20] and the absorption of H₂S with conventional solvents.

We are currently working to arrive at a better understanding of (i) the role of acidity and structural topology of the zeolite, and of the reaction conditions on the formation of products and (ii) the similarities and differences between M2TH and MTH catalyzed by zeolites.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.apcatb.2013.01.037>.

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